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SINTERING OF CORUNDUM MIXTURES MODIFIED BY A VITREOUS PHASE OF A EUTECTOID COMPOSITION

R. V. Zubashchenko[1] and I. I. Nemets[1]

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The effect of a vitreous phase of a eutectoid composition on sintering of corundum mixtures is considered. It is established that the additive corresponding to a eutectic composition of the CaO – Al_2O_3 system melting at a temperature of 1395°C improves the service properties of corundum concrete through activating its sintering.

Despite a general decrease in the production and consumption of refractories in recent years, the volume of production and use of unmolded refractories has been growing, which provides for substantial savings in energy, materials, and labor resources. Of all the kinds of unmolded refractories, the most common is low-cement refractory concrete (LCRC).

The main attention in the development of LCRC is focused on decreasing the content of CaO and improving its thermomechanical properties. The most common in the LCRC group are corundum and high-alumina concretes [1].

It is known that the properties of concrete change in heating. Phase and structural modification occur in heating refractory concrete (including corundum concrete). Three temperature intervals are arbitrarily distinguished: 600 – 1000, 1000 – 1600, and over 1600°C [2].

The processes observed in a temperature interval of 600 – 1000°C mainly represent thermal dissociation, in particular, dehydration of calcium hydroaluminates, which are responsible for loosening of traditional corundum concrete. Characteristic specifics of refractory concrete within the specified interval include high dispersion of crystalline formations, extended porosity, and minimum mechanical strength.

Within a temperature interval of 1000 – 1600°C highly active products of binder destruction undergo significant phase and structural transformations directed toward bringing the heterogeneous composition to an equilibrium state. The most important physicochemical processes in this temperature interval are sintering of refractory concrete and recrystallization of mineral phases. The final result of thermal treatment at average temperatures is the formation of a ceramic structure of refractory concrete providing for optimum physicochemical parameters.

[1] Belgorod State Technological Academy of Construction Materials, Belgorod, Russia.

At temperatures above 1600°C these transformations intensify and get completed.

Consequently, the role of the binder to a large extent is reduced to ensuring the necessary mounting strength of unmolded refractory after hardening and drying. A subsequent increase in mechanical strength occurs as a consequence of sintering. Accordingly, the following objectives are set intensifying the sintering process and obtaining lower porosity values.

One of the methods for intensifying the process of sintering is the introduction of a liquid phase into the system. For this purpose a low-melting component of a eutectoid composition (a eutectoid component) was introduced into corundum refractory, which, as a consequence of reaction with the refractory components, produced high-melting compounds.

An analysis of the phase diagrams of oxide systems indicates that the least low-melting eutectic which does not produce low-melting equilibrium phases as a consequence of its reaction with the components of corundum refractory (concrete) is a composition in the CaO – Al_2O_3 system with a melting point of 1395°C [3].

For experimental studies three refractory mixtures were prepared. The estimated content of CaO in all mixtures was equal to 2.0%.

Mixture	Cement content, %
I	7.5
II	5.0
III	2.5

Standard methods were used to determine the properties of the corundum refractories.

Testing was carried out with equal technological parameters: granular composition of the filler, specific surface area of mixed binder (5500 cm^2/g), ratio of filler to mixed binder,

amount of water (moisture 7.0%), vibration parameters (amplitude 0.5 mm, frequency 30 Hz), except for the ratio of the mixed binder components, provided the content of CaO remain constant.

The mixed binder in mixture I was represented by alumina and high-alumina cement, in mixtures II and III by alumina, high-alumina cement, and a eutectoid component, mixture III containing the highest amount of the eutectic component.

It should be noted that a constant content of CaO was ensured by a certain decrease in the quantity of high-alumina cement compared to mixture I, which clearly had an effect on the activity of the mixed binder.

The ratio between coarse and fine filler was determined based on the highest bulk weight of their mixture. The filler was electrocorundum of two fractions (3.0 – 0.5 mm and less than 0.5 mm). Variations in the ratio of the specified electrocorundum fractions showed that the highest bulk density (2.71 g/cm^3) was seen in the composition containing 70% fraction sized 3.0 – 0.5 mm and 30% fraction below 0.5 mm.

The maximum possible content of mixed binder (with a constant content of coarse and fine filler) was estimated based on shrinkage of concrete, since the main requirement of refractory concrete is constancy of volume.

In laboratory testing of the quality of unmolded refractories, their shrinkage in heating and subsequent exposure for 5 h at the service temperature should not exceed 1% [4]. The testing results indicated that shrinkage of samples containing over 25% mixed binder after firing at a temperature of 1650°C with a 5-h exposure exceeded 1%, which is not admissible.

Thus, an optimum ratio of the filler fraction of 3.0 – 0.5 mm to the filler fraction below 0.5 mm to the mixed binder is 52.5 : 22.5 : 25.0.

To identify the dependence of the properties of corundum refractories on the heat-treatment temperature, samples were fired at 1000, 1400, and 1650°C with an exposure for 1 h at each temperature, after which the open porosity and compression strength of samples were found.

It can be seen from the data in Table 1 that an increased content of the eutectoid component due to more intense sintering decreases the open porosity of the heat-treated refractory. In a mixture that did not contain the eutectoid component, open porosity changed from 15.2 to 14.3%, whereas in mixtures II and III it changed from 16.8 and 18.9, respectively, to 13.0 and 12.2%.

The refractory containing the highest amount of the eutectoid component after drying had the lowest compression strength. However, it should be noted that mechanical strength of dried unmolded refractory is not a determining criterion, since the solid lining of all types of thermal plants undergoes heating before service; therefore, the strength of a heat-treated refractory is a more significant characteristic. According to the data obtained, an increased content of the eutectoid component in the composition of corundum refractory increases the strength of heat-treated refractory. Thus, after samples were fired at 1650°C, the compressive strength of mixtures I, II, and III was equal to 68, 91, and 109 MPa, respectively (see Table 1).

TABLE 1

Parameter	Corundum refractory mixture		
	I	II	III
Open porosity, %, of samples after heat treatment at:			
110°C, 36 h	15.2	16.8	18.9
1000°C, 1 h	19.8	22.2	23.4
1400°C, 1 h	16.4	15.3	14.1
1650°C, 1 h	14.3	13.0	12.2
Compressive strength, MPa, of samples after heat treatment:			
110°C, 36 h	41	24	13
1000°C, 1 h	19	10	7
1400°C, 1 h	47	59	72
1650°C, 1 h	68	91	109

The heat resistance of refractories was determined on samples preliminarily treated at 1650°C with a 1-h exposure. The heat resistance of mixtures I, II, and III differed and amounted to 5, 7, and 8 thermal cycles, respectively.

After identifying the softening starting temperature it was established that a modification in the ratio of the mixed binder components did not change these parameters (1590 ± 20°C). The measurements were performed on samples fired at 1650°C with a 1-h exposure.

According to the x-ray phase analysis data, the high-melting compound synthesized under thermal treatment was calcium hexaaluminate $CaO \cdot 6Al_2O_3$, and synthesis of this compound was more intense in the presence of the eutectoid component.

Thus, using a low-melting eutectic of the $CaO – Al_2O_3$ system with a melting point of 1395°C as a sintering additive facilitates sintering of corundum concrete and leads to lower porosity values. An increased content of the eutectic additive does not have a perceptible effect on the softening starting temperature of the composition considered but raises it thermal stability.

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